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**FINAL REPORT: "CHEMISTRY AND TRANSPORT IN A MULTI-DIMENSIONAL MODEL"**

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The focus of the work funded under this proposal is the exchange between the stratosphere and the troposphere, and between the troposphere and the biosphere. These two interfaces represent the frontiers of atmospheric chemistry. It is the combination of exchange processes at both interfaces that ultimately controls how the biosphere (including human activities) affects the ozone layer. The modeling work was motivated by and attempts to integrate information obtained by aircraft, spacecraft, shuttle and oceanic measurements.

The model development and research activities accomplished in the past three years provide a technical and intellectual basis for the research in this group. The innovative part of our research program is related to the IAV of ozone and the hydrological cycle.

Other related but independently supported work include the study of isotopic fractionation of atmospheric species, *e.g.*, N<sub>2</sub>O and CO<sub>2</sub>. Our theory suggests that we now have the ability to probe the middle atmosphere at a level of sensitivity where subtle details such as the isotopic composition of simple molecules can yield measurable systematic effects. This creates the possibility for probing the chemistry and dynamics of the middle atmosphere using all of the N<sub>2</sub>O and CO<sub>2</sub> isotopologues.

In the following we will briefly describe the model development and review the highlights of recent accomplishments.

### **CALTECH/JPL CHEMICAL TRANSPORT MODEL DEVELOPMENT**

The Caltech/JPL chemical transport model (CTM) has considerable heritage since its initial development for applications to planetary and terrestrial atmospheres. More than ten Ph.D. theses have been written using this code, with each graduate student adding to the capability of the code. In the current operating mode it is a time dependent model of the global atmosphere in three dimensions (latitude, longitude, and altitude), composed of four modules: the chemical module, the solar radiative module, the infrared radiative module, and the transport module. Because of the modular design of the earlier 2-D model, the generalization to 3-D required only limited restructuring. The photochemical module, the solar radiative module, and the infrared

radiative module all were able to be used in the 3-D model as in the 2-D model, with only minor code adjustments.

It is a special feature of our model that the 1-D, 2-D and 3-D models are unified, with arbitrary dimensions in pressure, latitude and longitude. The current 2-D model has 18 latitudes, from pole to pole. There are 40 layers, from the surface to  $8.66 \times 10^{-3}$  hPa in a log pressure coordinate. The model includes the chemistry of the major catalytic cycles of  $\text{HO}_x$ ,  $\text{NO}_x$ ,  $\text{ClO}_x$ , and  $\text{BrO}_x$  and parent molecules such as  $\text{N}_2\text{O}$ ,  $\text{CH}_4$  and the CFC's. We use the NASA recommendations for stratospheric chemistry (Sander *et al.*, 2000). The circulation used is one computed from UARS data (Eluszkiewicz *et al.*, 1996). The model was used by Yung and Miller (1997), Miller and Yung (2000) and Blake *et al.* (2002). Recently, the 2-D model has been upgraded to 3-D. The model upgrade is designed to use 3-D wind fields, convection and other transport parameters from different sources, be they GCM outputs or the products of data assimilation systems. Therefore, the model resolution is variable and the vertical coordinate can be pressure, sigma or mixed sigma/pressure coordinates.

The current version of the 3-D model uses GISS GCM output (Rind, *et al.*, 1988) to drive the CTM transport. It has 46 latitudes, from pole to pole, 72 longitudes around the globe and 23 layers of mixed sigma/pressure coordinates from the surface to 0.02 hPa. The lowest 11 layers, which are below 150 hPa use sigma coordinates. The top 12 layers use pressure coordinates. One year GISS GCM outputs are used repeatedly. The winds and the convective fluxes are updated every 3 hours. Both dry and wet convection are included. The effects of entrainment and detrainment by convection are also calculated. In order to avoid the extremely small time step imposed by the Courant limit, the grid boxes near the poles are combined to form larger boxes. Using this scheme the time step for the transport is about half an hour. The outputs of the GISS GCM have been successfully used for several runs of CTM (Wild, *et al.*, 2000, Olsen, *et al.*, 2000, Hannegan, *et al.*, 1998 and Hartke and Rind, 1997).

The Caltech/JPL 3-D model has been tested to simulate the distributions of  $\text{N}_2\text{O}$  and  $\text{O}_3$ . In both cases, simplified photochemistry schemes are used.

## RESEARCH SUMMARIES

In this section we summarize the research results. A full list of our papers, conference presentations, and student training will follow in a later section.

### **Temporal and spatial patterns of the interannual variability of total ozone in the tropics**

The recently constructed dataset, combining the monthly mean column abundances collected by the Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscatter Ultraviolet (SBUV and SBUV/2) instruments, provides a nearly continuous record from late 1978 to 2000 on a  $5^\circ \times 10^\circ$  latitude-longitude grid. The precision and calibration of these measurements allow very small signals, ~1% of total column ozone, to be clearly seen. Using merged ozone data (MOD), we have carried out an empirical orthogonal function (EOF) study of the temporal and spatial patterns of the interannual variability of total column ozone in the tropics. The first four EOFs of our study capture over 94% of the variance of the deseasonalized data. The leading two EOFs, respectively accounting for 54% and 25% of the variance, display structures attributable to the quasi-biennial oscillation (QBO), with influence from a decadal oscillation (most likely the solar cycle). The third EOF (11% of the variance) represents an interaction between the QBO and an

annual cycle. The fourth EOF (4% of the variance) is related to the El Nino - Southern Oscillation. This is the first complete analysis of tropical ozone data using simultaneously the longitudinal, latitudinal and temporal patterns. A paper based on this work (Camp *et al.* 2002) is in review at *J. Geophys. Research*. The preprint may be viewed in <http://yly-mac.gps.caltech.edu/> under "O<sub>3</sub> Paper".

### **Isotope Compositions in the Upper Troposphere and Lower Stratosphere**

Observations of the isotopic ratio in H<sub>2</sub>O vapor can provide unique tests of the atmospheric physics that control dehydration. With improved H<sub>2</sub>O line lists and retrieval methods, we are able to estimate the water isotope abundances in the upper troposphere/lower stratosphere, especially for the tropics, using Fourier Transform InfraRed (FTIR) Interferometer data from the Atmospheric Trace Molecule Spectroscopy (ATMOS) and the Mark IV balloon flights. The results are summarized in Figure 2. The D/H ratio remains constant from 10 to 25 km (left panel), even though the mixing ratio of H<sub>2</sub>O changes by an order of magnitude (right panel). This provides definitive evidence for the tropical tropopause layer (TTL), first suggested by Sherwood and Dessler (2001). The details of this work may be viewed from our recent AGU presentation (Kuang *et al.*, 2001; <http://www.gps.caltech.edu/~kzm/HDO/>). Simultaneous retrieval of CO from the same spectra yields vertical profiles for this short-lived molecule. From this an estimate of the time constant of mixing in the TTL can be made.

### **Photo-induced isotopic fractionation**

This paper presented a systematic method for the analysis of photo-induced isotopic fractionation. The physical basis for this fractionation mechanism is that isotopic substitution alters energy levels, molecular symmetries, spin statistical weights, transition dipole moments and other fundamental molecular properties, producing spectroscopic signatures distinguishable from that of the parent isotopologues. These mass dependent physical properties are identical to those invoked by Urey to explain stable isotope fractionation in chemical systems subject to thermodynamic equilibrium. Photo-induced isotopic fractionation is a completely general phenomenon and should be observable in virtually all gas phase photochemical systems. Water photo-induced isotopic fractionation has been examined in detail using experimental and theoretical data. These results illustrate the salient features of this fractionation mechanism for molecules possessing continuous UV absorption spectra and unit photodissociation quantum yields. Using the photo-induced isotopic fractionation methodology in conjunction with standard photochemical models, we predict substantial deuterium enrichment of water vapor in the planetary atmospheres of Earth and planetary atmospheres. The paper has appeared in *J. Geophys. Res.* (Miller and Yung, 2000).

### **PUBLICATIONS SUPPORTED BY THIS GRANT**

R. L. Herman, C.R. Webster, R. D. May, D.C. Scott, H. Hu, E.J. Moyer, P.O. Wennberg, T. F. Hanisco, E.J. Lanzendorf, R.J. Salawitch, Y.L. Yung, J. J. Margitan, T.P. Bui., 1999, Measurements of CO in the Upper Troposphere and Lower Stratosphere. *Chemosphere-Global Change Sci.*, **1**, 173-183.

Y. L. Yung, C. Shia and R. L. Herman, 1999, Is the biomass burning source of CO decreasing? *Chemosphere*, **1**, 83-90.

Liao, H., Yung, Y. L., and Seinfeld, J. H., 1999, Effects of aerosols on tropospheric photolysis rates in clear and cloudy atmospheres. *J. Geophys. Res.*, **103**, 3781-3788.

C.E. Miller and Y.L. Yung, 2000, Photo-induced isotopic fractionation, *J. Geophys. Res.*, **105** 29039-29051.

C.D. Camp, M.S. Roulston, A.F.C. Haldemann, and Y.L. Yung, 2001, The sensitivity of tropospheric methane to the interannual variability in stratospheric ozone, *Chemosphere-Global Change Science*, **3**, 147-156.

Z. M. Kuang, J. S. Margolis, G. C. Toon, D. Crisp, and Y. L. Yung, 2002, Space-borne measurements of atmospheric CO<sub>2</sub> by high-resolution NIR spectrometry of reflected sunlight: A sensitivity Study, Submitted to *Geophys. Res. Lett.*

C. D. Camp, M. S. Roulston, and Y. L. Yung, 2002, Temporal and spatial patterns of the interannual variability of total ozone in the tropics, Submitted to *J. Geophys. Res.*

F.W. Irion *et al.*, 2002, The Atmospheric Trace Molecular Spectroscopy Experiment (ATMOS) Version 3 data retrievals, Submitted to *Applied Optics*.

#### **CONFERENCE PRESENTATIONS**

Z. Kuang, and Yung, Y. L. Interannual variability of the Earth's albedo as observed by TOMS. EOS transactions, AGU, OS51D, p.276, 1999.

F. W. Irion, *et al.*, ATMOS Version 3 retrievals of H<sub>2</sub>O, CH<sub>4</sub>, HDO and CH<sub>3</sub>D. EOS transactions, AGU, A12B, p.110, 1999.

F. P. Mills, *et al.*, Terrestrial mesosphere and comparison to OH column measurements from JPL Table Mountain Facility. AGU, A51D, p.267, 1999.

F. P. Mills, Sander, S. P., Cageao, R. P., Nemtchinov, V., Jiang, Y., Russell, J. M., Remsberg, E. E., LeBlanc, T., LeBlanc, T., Nedoluha, G., Allen, M. A., and Yung, Y. L., Intercomparisons of OH Column Measurements from the JPL Table Mountain Facility with Measurements of O<sub>3</sub> and H<sub>2</sub>O, EOS Transactions American Geophysical Union, Vol. 81, No. 48, A71B-13, p. F99, December 15-19, 2000.

C.G. Morgan, G.A. Blake, T. Rahn, and Y.L. Yung, 2001, Isotopic Fractionation of N<sub>2</sub>O in the Stratosphere Revisited, Paper presented at the 18<sup>th</sup> Informal Conference on Photochemical and Kinetics Process in the Atmosphere, February 20, California Institute of Technology, Pasadena, CA.

E. J. Moyer, *et al.*, 2001, Seasonal Variation in Episodic Rapid Meridional Transport in the Lowermost Stratosphere from in-situ Trace Gas Measurements, EOS Transactions American Geophysical Union, Vol. 81, No. 48, A42B-20.

Z. M. Kuang, *et al.*, 2001, Isotope Compositions in the Upper Troposphere and Inside the Polar Vortex, EOS Transactions American Geophysical Union, Vol. 82, No. 47, A12C-10.

J. Farrara, X. Jiang, S. S. Leroy, J. Feynman, A. Ruzmaikin, and Y. Yung, 2001, Effects of a Reduced Ozone Layer on the Lower Stratosphere and the Troposphere, AGU Fall Meeting, A11C-06, San Francisco, CA.

F. P. Mill, *et al.*, 2001, OH Column Abundance over JPL's Table Mountain Facility 1997-2000, EOS Transactions American Geophysical Union, Vol. 82, No. 47, SA41B-0725, p.219, December 10-14, 2001.

Y. Jiang, Y. L. Yung, S. P. Sander, and L. D. Travis, 2001, Modeling of Atmospheric Radiative Transfer with Polarization and Its Application to the Remote Sensing of Tropospheric Ozone, EOS Transactions American Geophysical Union, Vol. 82, No. 47, A21B-0074, p.119, December 10-14, 2001.

C. D. Camp, M. S. Roulston, and Y. L. Yung, 2001, Spatiotemporal Patterns of the Interannual Variability of Total Column Ozone in the Tropics, EOS Transactions American Geophysical Union, Vol. 82, No. 47, A42A-0082, p.226, December 10-14, 2001.

**PH.D THESIS STUDENTS SUPPORTED BY THIS GRANT:**

E. J. Moyer, Tracers of Rapid Transport in the Lower Stratosphere, 2001, California Institute of Technology.

Z. M. Kuang, Water Isotopes as Tracers in the Upper Troposphere, 2002, California Institute of Technology.